

Assembly, Testing, and Operation of Laboratory Distilling Columns of High Efficiency¹

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A description is given of the assembly, testing, and operation of the laboratory distilling columns used at the National Bureau of Standards in the work of the American Petroleum Institute Research Project 6 on the analysis and purification of hydrocarbons and in the work on the preparation of NBS Standard Samples of hydrocarbons. The following topics are covered: Assembly of distilling columns, including pot, rectifying section, jacket, head, reflux regulator, receiving assembly, electrical heating system, thermometric systems, and controlled-pressure system; testing of distilling columns, including test mixtures and results; and operation of columns, for both regular and azeotropic distillations. Drawings of the equipment and apparatus are given, including the arrangement of the 15 distilling columns, measuring instruments, and auxiliary equipment in the distillation room. A view of the distillation room is given.

I. Introduction

This report describes the assembly, testing, and operation of the laboratory distilling columns used at the National Bureau of Standards in the work of the American Petroleum Institute Research Project 6 on the analysis and purification of hydrocarbons and in the work on the preparation of NBS Standard Samples of hydrocarbons.

These distilling columns have charging capacities ranging from $\frac{1}{2}$ to 15 liters, with separating efficiencies in the range of 100 to 200 equivalent theoretical plates at total reflux. The distilling operations are performed continuously 24 hours a day, 7 days a week, with reflux ratios from 125/1 to 180/1 and rates of removal of product ranging from $\frac{1}{2}$ to 12.5 ml of liquid an hour. The total time of distilling given charges ranges up to 1,800 hours.

Drawings of the equipment and apparatus are given, including the arrangement of the 15 distilling columns, measuring instruments, and auxiliary equipment in the distillation room.

¹ This investigation was performed at the National Bureau of Standards mainly as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.

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II. Assembly of Distilling Columns

1. Complete Assembly of Individual Column

Figure 1 shows a complete assembly of the main part of one of the distilling columns. All the glass parts of the column proper are sealed together, making one continuous closed system of glass from the pot to the receiver. Details of the assembly are given in the legend of figure 1 and in the following text.

Figure 2 gives the details of the mounting of the transite blocks (constituting the support for the glass pot) on the angle iron brackets (constituting the main support of the column). The position of the horizontal angle iron and supporting brackets on the wall of the room is shown.

2. Details of Individual Column

(a) Pot

Figure 3 gives the details of the 7-liter glass pot.

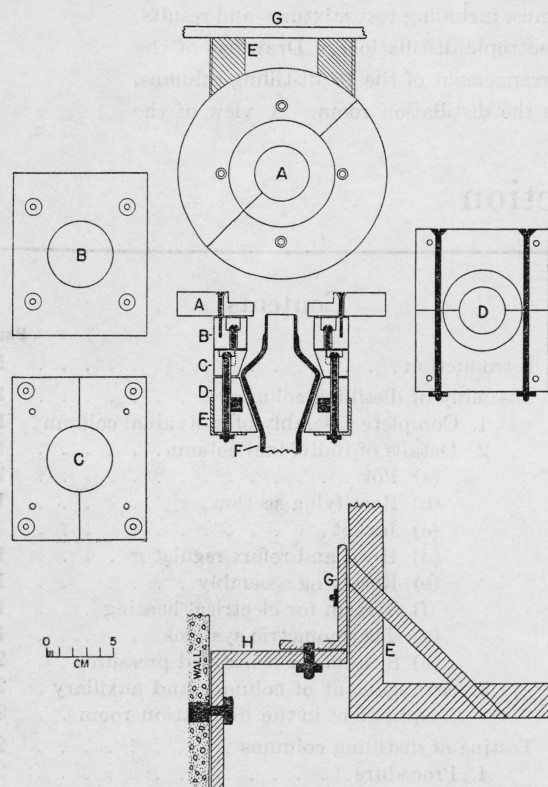


FIGURE 2.—*Transite blocks and metal bracket support for 7-liter still pot.*

A, B=transite blocks supporting jacket assembly.

C, D=transite blocks supporting glass still pot.

E =angle iron bracket supporting transite blocks.

F = neck of glass still pot.

G =angle iron running horizontally around room. (See fig. 12.)

H =brackets supporting angle iron G . (See fig. 12.)

The transite blocks for supporting this pot are shown in figure 2 and the details of the pot assembly are given in figure 1.

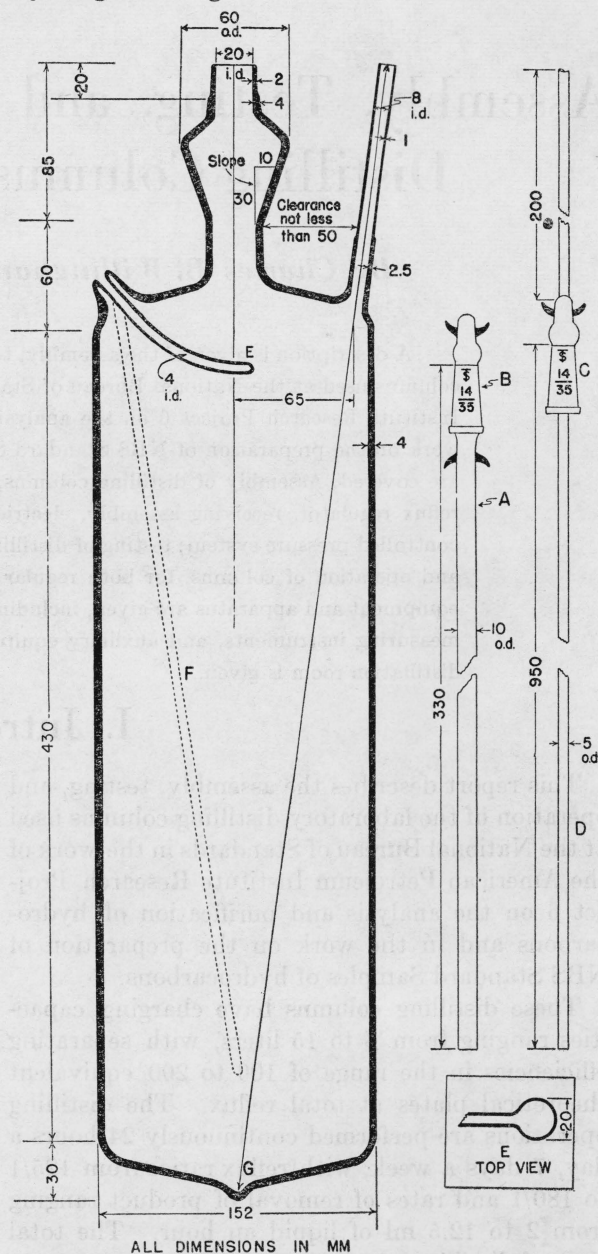


FIGURE 3.—Details of the 7-liter glass still pot.

The material is Pyrex laboratory glass.

A=filling tube, to be sealed to tube extending from pot.

B =cap of filling tube.

C=cap of withdrawal tube.

D=withdrawal tube.

E=tube for thermoelement.

F = position of tube for thermoelement, in earlier design.

G=recess in bottom of pot, to permit complete removal of undistilled material through the withdrawal tube.

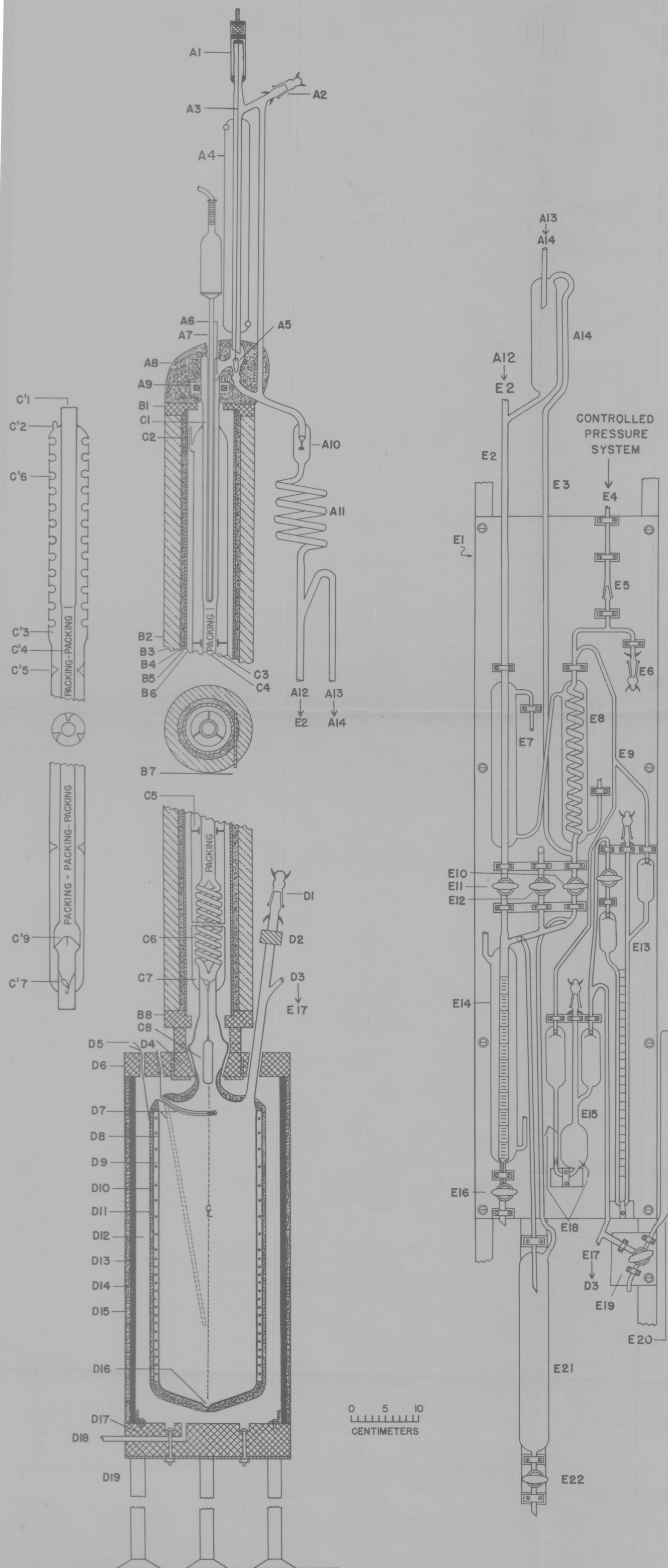


FIGURE 1.—Assembly of distilling column.

- A = head and reflux regulator [1] (For details, see figs. 6 and 8).
A1 = metal regulator with metallic bellows [2].
A2 = capped opening, with standard ground joint 12/30.
A3 = tungsten rod, No. 12 A.W.G.
A4 = condenser.
A5 = ground-glass valve.
A6 = apron.
A7 = platinum resistance thermometer.
A8 = thermal insulation.
A9 = transite collar for lateral support.
A10 = drop counter.
A11 = expansion spiral.
B = jacket assembly (see also fig. 7).
B1 = transite closure.
B2 = aluminum foil.
B3 = magnesia insulation.
B4 = electrical resistance heating wire, Nichrome, asbestos covered.
B5 = metal tube, steel or aluminum, split vertically, in two longitudinal sections, insulated with a silicone resin and asbestos paper.
B6 = air gap.
B7 = thermometer well, steel or aluminum, brazed to tube B5.
B8 = transite supports.
C = rectifying section for Heli-Grid packing.
C1 = open section for thermometer well.
C2 = seal-off tube for evacuated, silvered, jacket of rectifying tube.
C3 = wall of rectifying tube proper, showing depth of thermometer well and height of packing.
C4 = packing, Heli-Grid.
C5 = lateral support for rectifying tube proper (see also fig. 7).
C6 = double helix expansion section at bottom of rectifying tube proper.
C7 = throat to direct liquid to center.
C8 = drop counter.
C9 = rectifying section for packing of helices.
C10 = open section for thermometer well.
C11 = seal-off tube for evacuated, silvered, jacket of rectifying tube.
C12 = wall of rectifying tube proper, showing depth of thermometer well and height of packing.
C13 = packing, stainless-steel helices 3/32 inch in diameter of No. 30 A.W.G. wire.
C14 = indentations in jacket for centering rectifying tube.
C15 = expansion bellows for jacket of rectifying tube.
C16 = throat to direct liquid to center.
C17 = support for packing, conical spider with four legs.
D = still pot assembly (see also figs. 3 and 4).
D1 = opening for introduction of charge, standard ground joint 14/35.
D2 = main support for charging tube.
D3 = tube connecting pot to manometer E17.
D4 = main support for glass still pot and rectifying tube (see also figs. 2 and 5).
D5 = electrical leads to heaters for still pot.
D6 = removable cover.
D7 = thermometer well.
D8 = Pyrex-glass pot (4-mm wall).
D9 = special Glascol heater.
D10 = asbestos insulation.
D11 = aluminum foil.
D12 = air gap.
D13 = cylinder (Pyrex glass or sheet metal).
D14 = asbestos insulation.
D15 = aluminum foil.
D16 = well for removal of residue.
D17 = transite base.
D18 = compressed-air line for cooling pot assembly.
D19 = metal stand.
E = receiving assembly.
E1 = transite board.
E2 = product line from head A12.
E3 = controlled-pressure line to head A13.
E4 = copper line to controlled-pressure system.
E5 = copper to glass standard taper joint.
E6 = outlet to atmosphere, standard ground-glass joint 12/30.
E7 = condenser for cooling product line, near 10° C.
E8 = spiral condenser between receiver E14 and controlled-pressure system, near 10° C.
E9 = connection to manometers E13 and E15 from head A through spiral condenser E8.
E10 = stopcock between receiver E14 and controlled-pressure system.
E11 = stopcock on product line.
E12 = outlet from receiver E14 to atmosphere.
E13 = manometer (diethylene glycol monobutyl ether).
E14 = receiver, graduated, water-jacketed.
E15 = manometer (mercury, with tungsten contacts).
E16 = stopcock at bottom of receiver E14.
E17 = connection to manometers from pot D.
E18 = tungsten contacts.
E19 = stopcock for adding inert gas to manometer tube (E17 to D3).
E20 = overflow receiver.
E21 = stopcock at bottom of overflow receiver.

Figure 4 shows the details of the 18-liter glass pot. Figure 5 shows the details of the transite blocks for supporting the 18-liter glass pot. One of the important requirements in the manufacture² of these glass pots is that of thorough annealing. The transite blocks are made to fit the tapered neck of each individual pot. In the mounting of the pot in the transite block support, wet asbestos paper ($\frac{1}{64}$ inch thick) is placed around the

Technical drawing of a mechanical part, Figure 4, showing a top view and a side view. The top view is a large, irregular shape with a central circular feature and a small rectangular feature at the top. The side view shows a profile with a curved top and a flat bottom. Dimensions are given in millimeters. The top view has a total width of 229 mm and a total height of 655 mm. The side view has a total height of 950 mm. A detail view of the top view shows a circular feature with a diameter of 20 mm and a central hole with a diameter of 10 mm.

in figure 6. The place of sealing the head to the rectifying section is shown at *X* in figure 6.

(c) Jacket

The jacket surrounding the vacuum jacketed rectifying section over its entire length is shown

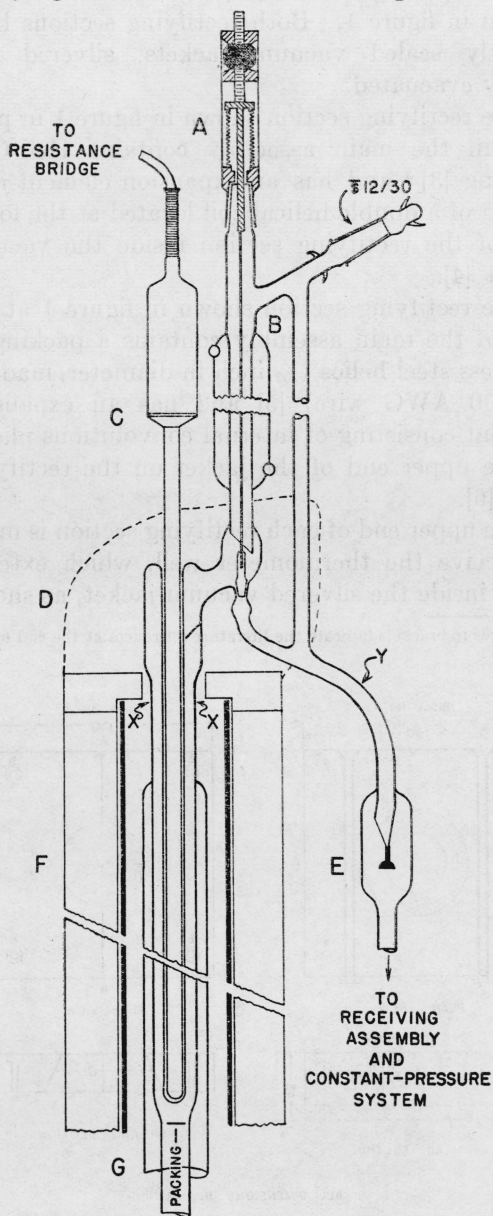


FIGURE 6.—Assembly of head of distilling column.

A=metal housing and control, with metallic bellows, as described in figure 3 of reference [2].

B=Pyrex-glass part of the apparatus.

C=platinum-resistance thermometer.

D=boundary of the thermal insulation on the finished head.

E=drop counter, with dimensions as shown in figure 2 of reference [2].

F=top of jacket assembly.

G=top of rectifying section, showing vacuum jacket.

X, *Y*=places where the glass head is sealed to the rectifying section and to the drop counter, respectively.

in figures 1 and 6 and in cross section in figure 7. The metal tube, steel or aluminum, carries the insulated heating wire.

(d) Head and reflux regulator

The head and reflux regulator has been described previously [1], and is shown in assembly form in figures 1 and 6. Figure 8 shows the details of the glass part of the head and reflux regulator, with dimensions revised over those previously reported.

(e) Receiving assembly

The receiving assembly is shown in figure 1. Details are given in the legend of figure 1. The tungsten contacts are conditioned as described in part II of reference [7].

(f) System for electrical heating

The system for electrical heating of the pot and jacket, and for controlling the pot heater, is shown in figure 9 in diagram.

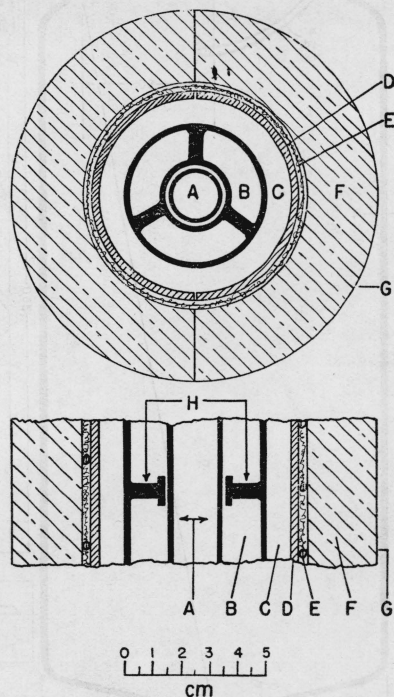


FIGURE 7.—Cross section of the jacket assembly.

A=rectifying tube.

B=jacket of rectifying tube, silvered and evacuated.

C=air gap.

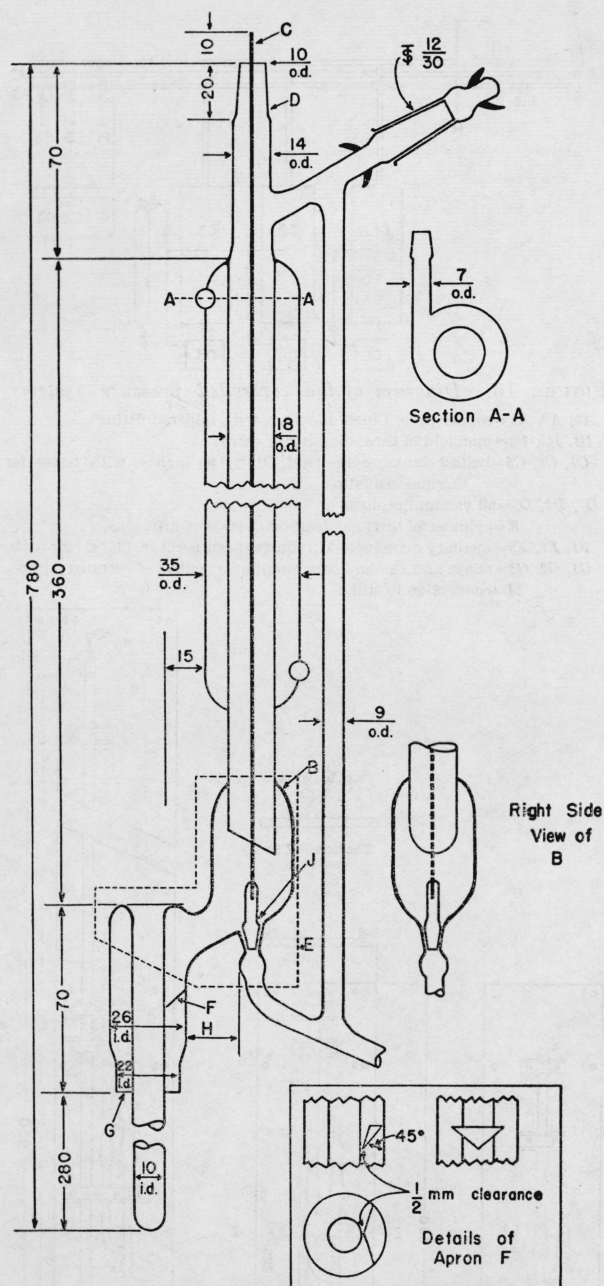
D=metal tube, steel or aluminum, split longitudinally in two sections.

E=electrical resistance heating wire, Nichrome.

F=thermal insulation (85% magnesia).

G=aluminum-foil covering.

H=glass support for centering rectifying tube.



ALL DIMENSIONS IN MM

FIGURE 8.—Details of the glass part of the distilling-column head.

- A=section showing opening in jacket of condenser.
 B=portion connecting condenser with ground-glass valve.
 C=tungsten rod, No. 12 AWG.
 D=male ground joint, standard taper, 12/20.
 E=portion having extra-heavy wall.
 F=apron to direct liquid from the condenser to the thermometer well.
 G=bottom edge for sealing to rectifying tube (should be smooth and have its plane perpendicular to the axis of the thermometer well).
 H=clearance to be not less than 15 mm.
 J=ground-glass valve, taper 1 in 5, small end 4 mm, large end 6 mm, length 10 mm, ground for high vacuum. Material is Pyrex laboratory glass.

(g) Thermometric systems

The thermometric systems are shown in diagram in figure 9.

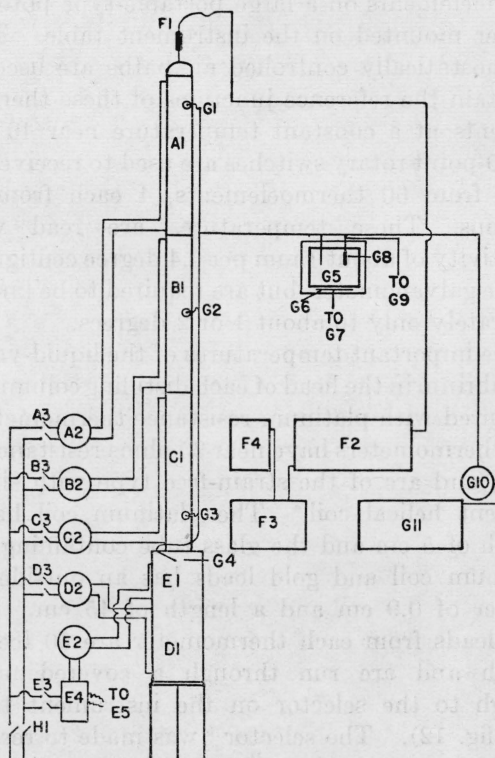


FIGURE 9.—Diagram of the electrical heating and thermometric systems.

A1, B1, C1=electrical heaters (300 watts, 110 volts a-c) for the top, middle, and bottom sections, respectively, of the jacket of the rectifying section.

D1, E1=lower and upper electrical heating units of sleeve-type Glascol heating mantle.

A2, B2, C2, D2, E2=variable transformers, 5 amperes, 110 volts, a-c.

A3, B3, C3, D3, E3=double-pole, single-throw switches.

E4=relay, enclosed mercury contacts with vacuum-tube circuit.

E5=mercury manometer with tungsten contact points (E15, fig. 1).

F1=platinum-resistance thermometer, 25 ohms, research grade.

F2=thermometer selector, for 19 thermometers with 4 leads each.

F3=resistance bridge, Mueller type.

F4=galvanometer.

G1, G2, G3=single-junction copper-constantan thermoelements for the top, middle, and bottom sections, respectively, of the metal tube surrounding the rectifying section.

G4=single-junction copper-constantan thermoelement for the still pot.

G5=reference junction for thermoelements, in constant-temperature air bath (40° C).

G6=space heater, 200 watts, 110 volts, a-c.

G7=variable transformer, 5 amperes, 110 volts, a-c.

G8=mercury-in-glass thermoregulator.

G9=relay, enclosed mercury contacts, with vacuum-tube circuit.

G10=selector switches.

G11=potentiometer.

H1=double-pole, single-throw switch on constant-voltage supply line.

The temperatures in the pot and at the top, middle, and bottom of the metal jacket tube are measured with single-junction copper-constantan thermoelements on a large portable-type potentiometer mounted on the instrument table. Two thermostatically controlled air baths are used to maintain the reference junctions of these thermoelements at a constant temperature near 40° C. Six 10-point rotary switches are used to receive the leads from 60 thermoelements, 4 each from 15 columns. These temperatures are read with sensitivity of about 1 mm per 0.4 degree centigrade on the galvanometer, but are required to be known accurately only to about 1 or 2 degrees.

The important temperatures of the liquid-vapor equilibrium in the head of each distilling column are measured with platinum resistance thermometers. The thermometers have near 25 ohms resistance at 0° C, and are of the strain-free type with single filament helical coil.⁴ The platinum coil has a length of 5 cm and the glass tube containing the platinum coil and gold leads has an outside diameter of 0.9 cm and a length of 45 cm. The four leads from each thermometer are 50 feet in length and are run through a covered metal trough to the selector on the instrument table (see fig. 12). The selector⁵ was made to receive as many as 76 leads, 4 from each of 19 different thermometers.⁵ The resistance of the thermometer picked out with the selector is measured on a Mueller-type bridge,⁶ of special design, with an internal commutator. On this bridge, the smallest units are 0.001 ohm, and the resistance of a given thermometer is measured to the nearest 0.001 ohm or 0.01 degree centigrade, with the sensitivity on the galvanometer scale being near 1 mm per 0.01 degree centigrade.

In normal operation, in analytical distillations of wide boiling (25° to 175° C) charges, it is found that the temperature of the liquid-vapor equilibrium in the head of the distillation column is "smooth" within ± 0.01 degree centigrade. During distillations of highly purified hydrocarbons, it is usual for the temperature of the liquid vapor equilibrium in the head to be constant within ± 0.01 degree centigrade for several hundred hours.

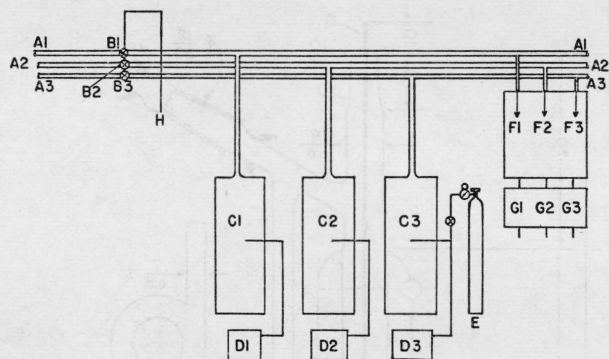


FIGURE 10.—Diagram of the controlled pressure systems.

A1, A2, A3=copper pipe, 1-inch diameter, with soldered fittings.

B1, B2, B3=manifold of three-diaphragm valves.

C1, C2, C3=ballast tanks, cylindrical, 21 by 60 inches, with cover for thermal insulation.

D1, D2, D3=oil vacuum pumps.

E=cylinder of inert gas (carbon dioxide or nitrogen).

F1, F2, F3=mercury manometers in constant-temperature (35° C) air bath.

G1, G2, G3=relays and vacuum tube circuits for control of vacuum pumps.

H=connection to still.

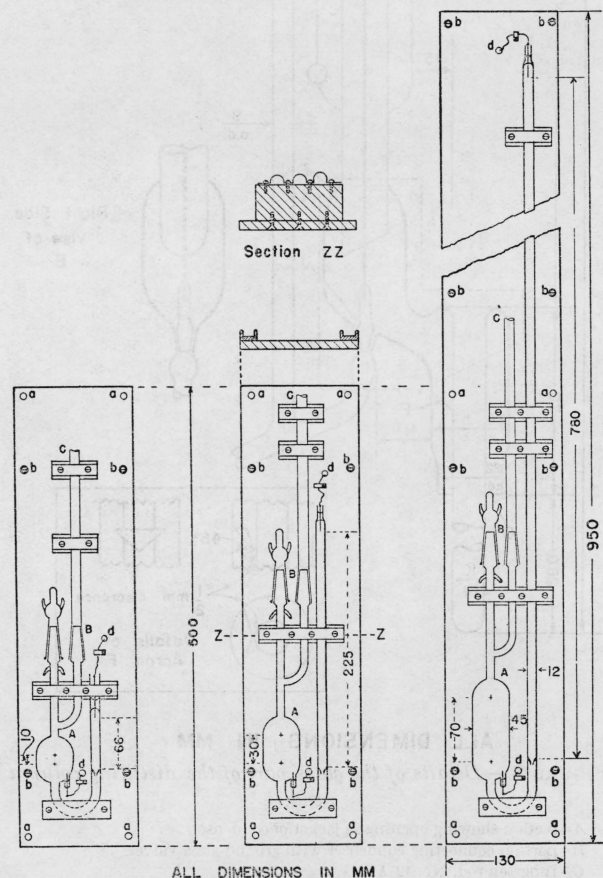


FIGURE 11.—Details of the mercury manometer assembly for the controlled pressure systems.

A=manometer proper, Pyrex glass.

B=standard taper (12/30) joint, copper female to glass male [8].

C=copper tube to controlled pressure system.

a =holes for mounting to main frame (not shown).

b=bolts holding transite to channel bars.

d=holes for leads to tungsten contacts.

⁴ Twenty of these platinum resistance thermometers were made for this installation by C. H. Meyers.

⁵ The selector and bridge were designed by E. F. Mueller and C. H. Meyers of this Bureau, and manufactured by the Rubicon Co., Philadelphia, Pa.

⁶ See footnote 5.

(h) System for controlled pressures

The system for controlling the pressures during the distilling operations is shown in diagram in figure 10. The details of the mercury manometers used in controlling the pressures constant at given values are shown in figure 11. The operation of the system for controlling pressures is essentially identical with that previously described in another report from this laboratory [7]. All of the connections and joints in the system, including one metal to glass tapered joint [8] at each controlling manometer (*B*, fig. 11) and at the receiving assembly on each distilling column (*E5*, fig. 1), are soldered.

From hourly observations of temperature made over long periods of time during many distillations of highly purified hydrocarbons at a controlled pressure of 724.5 mm Hg, it is found that the immediate variations in pressure at the head of the column during the operation of the vacuum

pump, as well as the long-time changes in the controlled pressure, normally do not exceed about ± 0.2 mm Hg.

The three controlled pressures normally maintained in the laboratory are 725, 217, and 57 mm Hg.

3. Arrangement of Columns and Auxiliary Equipment in the Distillation Room

Figure 12 gives a plan view of the first and second floor levels of the distillation room, together with a view of one wall, showing the location of the various services. The positions of the 15 distilling columns and of the auxiliary equipment are indicated. Figure 13 shows a view in the distillation room, including the instruments for the thermometric systems and the lower part of columns 5 to 10, inclusive.

III. Testing of Distilling Columns

1. Procedure

In this work, the testing of the distilling columns was performed under conditions similar to those encountered in actual operation. (See section IV.)

After equilibrium was established, with the column operating at total reflux, at the prevailing atmospheric pressure, small samples (about 2-ml in volume) were removed from the pot and head. The compositions of these samples were determined from measurements of refractive index. Twenty-four or more hours was allowed for the establishment of equilibrium in these tests.

The pressure drop through the column, from pot to head, was measured on the oil and mercury manometers in the receiving assembly (*E13* and *E15*, fig. 1).

The "through-put" was measured at the head of the column by collecting all the condensate formed in the condenser in a given time, usually 60 seconds or less. In these experiments, the head used was that described in reference [2].

2. Test Mixtures

For convenience in this and other investigations involving the use of mixtures of (a) *n*-heptane and methylcyclohexane and (b) 2,2,4-trimethylpentane and methylcyclohexane as test mixtures, values of refractive index as a function of composition were

determined experimentally for these two mixtures. Known mixtures of the pure components were made up accurately by weight. The refractive index, n_D , at 25° C, of these known mixtures was measured, by reference to the refractive index of the pure components, to the nearest 0.0001 on an Abbe-type refractometer graduated directly to 0.0001. For the system *n*-heptane and methylcyclohexane, 26 mixtures were made up and measured. For the system 2,2,4-trimethylpentane and methylcyclohexane, 26 mixtures were also made up and measured. The results, expressed as the difference between the refractive index of the mixture and of *n*-heptane or of 2,2,4-trimethylpentane, are as follows:

For *n*-heptane and methylcyclohexane, at 25° C,

$$n_D(\text{mixture}) - n_D(n\text{-heptane}) = 0.0306N + 0.0048N^2, \quad (1)$$

where n_D is the refractive index and N is the mole fraction of methylcyclohexane in the mixture. (See reference [20].)

For 2,2,4-trimethylpentane and methylcyclohexane, at 25° C,

$$n_D(\text{mixture}) - n_D(2,2,4\text{-trimethylpentane}) = 0.0244N + 0.0072N^2, \quad (2)$$

where n_D is the refractive index and N is the mole fraction of methylcyclohexane in the mixture.

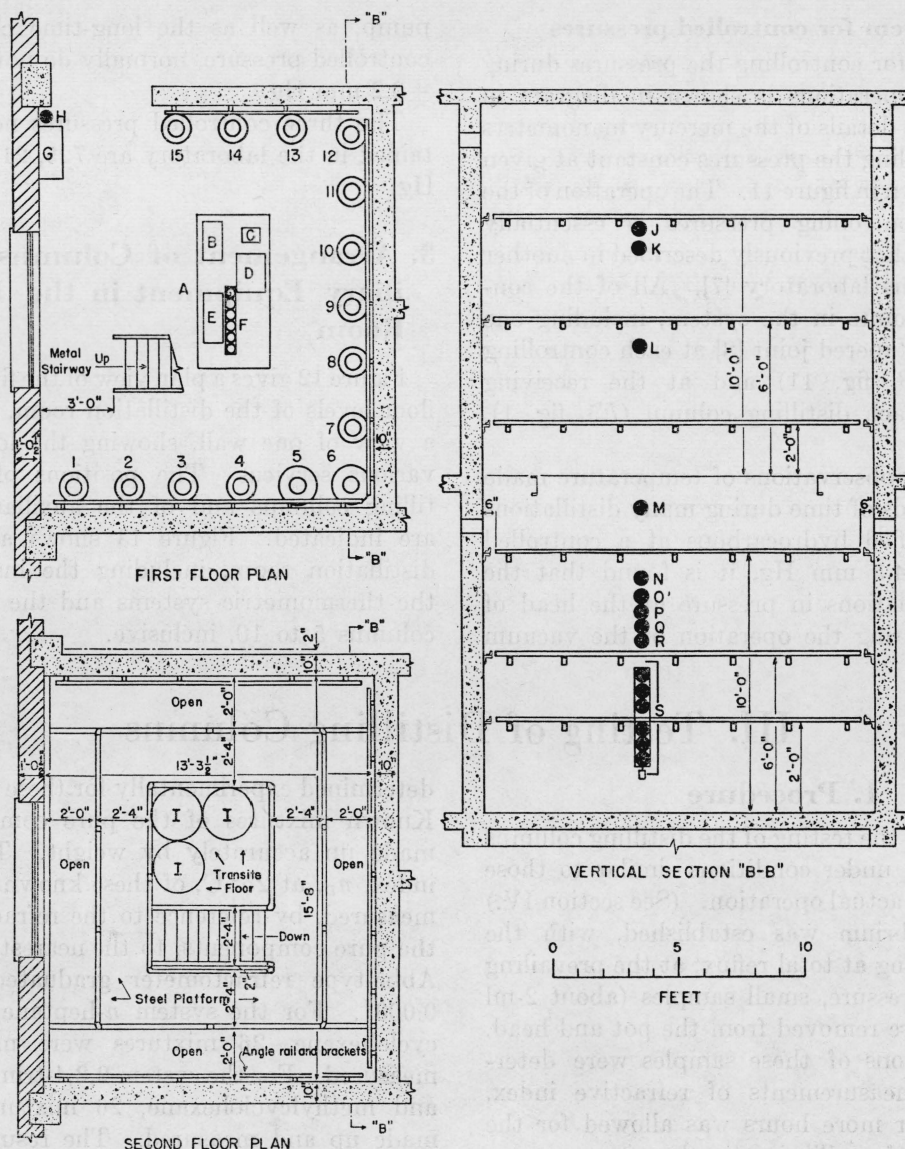


FIGURE 12.—Arrangement of the distilling columns, auxiliary apparatus, and services in the distillation room.

Plan views at the first- and second-floor levels, and a vertical view of one wall, are shown. The second-floor level has a 24-inch opening running around the four walls, a 28-inch metal walk with metal stairway to the first-floor level, and a center part covered with transite (on I-beams) for supporting the reservoir tanks of the controlled pressure systems.

The numbers adjoining the open double circle shown at three of the walls in the first-floor plan indicate the location of distilling columns 1 to 15. In each case, the larger circle shows the outside diameter of the pot assembly, and the inner circle shows the outside diameter of the jacket assembly. In the first-floor plan, the letters indicate the following:

- A = table for mounting instruments.
- B = resistance bridge.
- C = galvanometer.
- D = thermometer selector, for platinum-resistance thermometers.
- E = potentiometer.
- F = multiple switches for thermoelements.
- G = pumps, manometers, relays, etc., for the controlled-pressure systems.

H = cylinder of carbon dioxide or nitrogen gas, for the controlled-pressure system.

In the second-floor plan, the letters *I* show the location of the three large reservoirs for the controlled-pressure system. The distilling columns have not been shown in the second-floor plan, for simplicity.

In the vertical section, "B-B", the solid circles show the location of the various services for one distilling column, as follows:

- J = electric power outlet, 110 volts, a-c.
- K, M = water outlet, house line.
- L, N = drain, for discharged water.
- O = connection to manifold of three valves, one to each controlled-pressure system.
- P = refrigerated water, near 10°C.
- Q = compressed air.
- R = vacuum, house line.
- S = battery of electric power outlets, 110 volts, a-c.

Each of the 15 distilling columns is provided with a similar set of services.

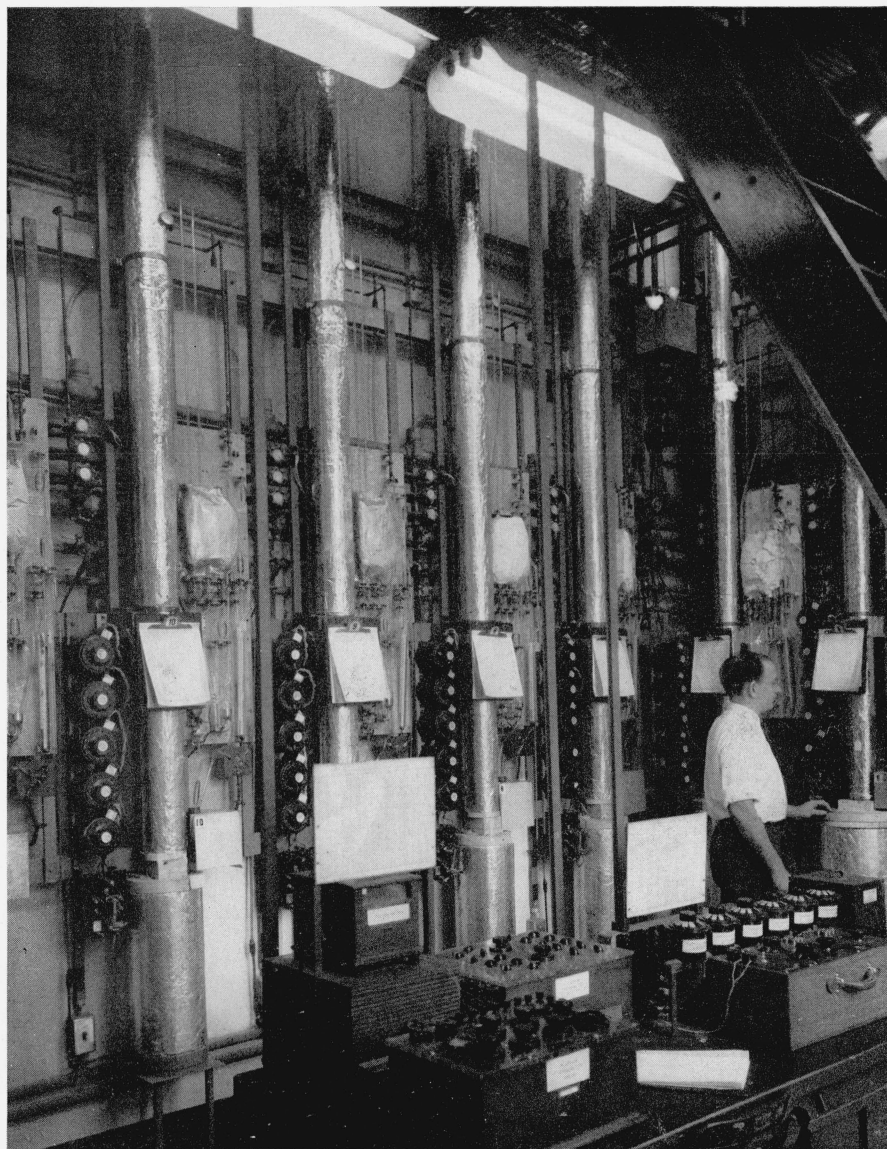


FIGURE 13.—View in the distillation room, showing the instruments for the thermometric systems and the lower part of columns 5 to 10, inclusive.

The foregoing equations reproduce each of the experimentally observed values of refractive index within ± 0.0001 .

The purified hydrocarbons used in this work for making up the foregoing known mixtures for measurements of refractive index, and also for making up the mixtures for testing the distilling columns, were from lots of purified *n*-heptane, 2,2,4-trimethylpentane, and methylcyclohexane having a purity substantially identical with the same compounds described in another report from this laboratory [9], namely, *n*-heptane, 0.9993, 2,2,4-trimethylpentane, 0.9988, and methylcyclohexane, 0.9990 mole fraction.

The number of equivalent theoretical plates, n , in the actual rectifying section was calculated from the equation [10, 11]

$$n+1 = [1/\log (P_A^\circ/P_B^\circ)] \log [(N_A/N_B)_{\text{head}}/(N_A/N_B)_{\text{pot}}], \quad (3)$$

where P° is the vapor pressure of the given component in the pure state at the mean temperature, N is the mole fraction of the given component in the liquid phase in the head or pot as indicated, A is the more volatile component, and B is the less volatile component.

Assuming that the two components in the binary mixtures are substantially ideal as regards the relation of vapor pressures to composition. (See references [18, 19]), the data on the vapor pressures of the pure components recently reported from this laboratory [7] were reduced to give values of P_A°/P_B° in the neighborhood of the normal boiling points of the components. From these data, P_A°/P_B° for *n*-heptane and methylcyclohexane has the values of 1.0738₀ at the normal boiling point of *n*-heptane (98.426° C) and 1.0758₄ at the normal boiling point of methylcyclohexane (100.934° C). For the 2,2,4-trimethylpentane and methylcyclohexane, these data yield values of P_A°/P_B° equal to 1.0492₂ at the normal boiling point of 2,2,4-trimethylpentane (99.238° C) and 1.0489₀ at the normal boiling point of methylcyclohexane (100.934° C).

With these values, and corresponding ones for neighboring temperatures, eq 3 giving the number of equivalent theoretical plates may be written as follows for the two mixtures:

For *n*-heptane and methylcyclohexane, in the range 96½° to 101½° C,

$$n+1 = [32.15 - 0.34(t-99)] \log [(N_A/N_B)_{\text{head}}/(N_A/N_B)_{\text{pot}}]. \quad (4)$$

For 2,2,4-trimethylpentane and methylcyclohexane, in the range 97° to 101½° C,

$$n+1 = [48.07 + 0.13(t-100)] \log [(N_A/N_B)_{\text{head}}/(N_A/N_B)_{\text{pot}}]. \quad (5)$$

In eq 4 and 5, t is the mean temperature in degrees centigrade. The numerical coefficients are estimated to have uncertainties not greater than about $\pm \frac{1}{2}$ percent for the ranges given.

In connection with the full-scale testing of columns having 200 or more theoretical plates, the authors consider the following binary mixtures as being suitable for trial:

(a) 2,3,4-Trimethylpentane and 2,3,3-trimethylpentane, with normal boiling points of 113.467° and 114.760° C, a difference of 1.293° C [7];

(b) 2,5-Dimethylhexane and 2,4-dimethylhexane, with normal boiling points of 109.103° and 109.429° C, a difference of 0.326° C [7]. From the data on vapor pressures recently reported on these compounds [7], and making the assumption of ideality as previously done above, the values of the constants of eq 3 applicable to these foregoing two test mixtures become as follows:

For 2,3,4-trimethylpentane and 2,3,3-trimethylpentane, over the range 111½° to 115° C,

$$n+1 = [64.95 - 0.36(t-114)] \log [(N_A/N_B)_{\text{head}}/(N_A/N_B)_{\text{pot}}]. \quad (6)$$

For 2,5-dimethylhexane and 2,4-dimethylhexane, over the range 107° to 110° C,

$$n+1 = [250.5 - 1.7(t-109)] \log [(N_A/N_B)_{\text{head}}/(N_A/N_B)_{\text{pot}}]. \quad (7)$$

As before, t is the mean temperature in degrees centigrade. The numerical constants have uncertainties estimated to be less than about $\pm \frac{1}{2}$ percent for the trimethylpentanes and about ± 3 percent for the dimethylhexanes.

Small samples (2 to 5 ml) of each of the foregoing binary mixtures may be readily analyzed with sufficient accuracy by means of infrared spectrometers. For the calibration of spectrometers for such analyses, small samples of these compounds of known high purity are available as NBS Standard Samples of hydrocarbons.⁷

Unfortunately, 2,5-dimethylhexane and 2,4-dimethylhexane are not at the present time available in sufficient quantity of adequate purity

⁷ A complete list of the hydrocarbons available as NBS Standard Samples may be obtained by writing to the National Bureau of Standards, Washington 25, D. C.

for use in testing distilling columns, nor are pure mixtures of the two compounds available.

With regard to 2,3,4-trimethylpentane and 2,3,3-trimethylpentane, the situation is more favorable. Although neither compound is available separately in sufficient quantity of high purity, pure binary mixtures of the two compounds may be readily obtained by efficient distillation of a commercial mixture (alkylate) of branched-chain paraffins. (See figs. 17 and 18.) In such case (referring to figs. 17 and 18), the fractions to be used in making up the test mixtures would consist of the fractions of distillate containing about 85 percent 2,3,4-trimethylpentane and 15 percent 2,3,3-trimethylpentane and running through to those fractions of distillate containing about 10 percent 2,3,4-trimethylpentane and 90 percent 2,3,3-trimethylpentane. In the example just cited, about 700 ml of material free of components

other than the two desired trimethylpentanes would have been obtained in a state suitable for blending for use as a test mixture.

3. Results

In figures 14, 15, and 16 are plotted the results of tests of rectifying sections 10, 15, and 25 mm in diameter and near 2.8 m in length, packed with stainless steel helices [5] ($\frac{3}{32}$ inch in diameter, made of No. 30 AWG wire). Results are given for the number of equivalent theoretical plates and the pressure drop per meter length of rectifying section, as a function of the through-put. The data are substantially in accord with observations on the same packing reported by Fenske and his collaborators [12, 13, 14].

Tests made on a rectifying section 13 mm in diameter and 1.83 m in length containing Heli-Grid packing [3] yielded the following results at atmospheric pressure: Number of equivalent theoretical plates at total reflux, 94, with a pres-

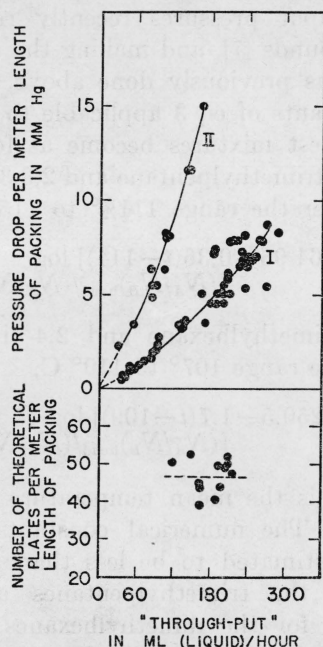


FIGURE 14.—Results of performance tests on rectifying section of 10-mm diameter packed with stainless-steel helices.

The upper scale of ordinates gives the pressure drop, in mm Hg, per meter length of packing; the lower scale of ordinates gives the number of equivalent theoretical plates per meter length of packing; and the scale of abscissas gives the "through-put" in milliliters (liquid) per hour. The rectifying section of the distilling column in which tests were made was 10 mm in inside diameter and 2.79 m in length, and was packed with stainless-steel helices, $\frac{3}{32}$ inch in diameter, of No. 30 AWG wire [5]. The test mixture was methylcyclohexane plus 2,2,4-trimethylpentane. For the pressure drop, curves I and II give results for controlled pressures of 770 mm and 217 mm Hg, respectively, at the head of the column. The mean value of the number of equivalent theoretical plates is 46.9, with an average deviation of ± 3.7 . Determination of the number of equivalent theoretical plates was made at the prevailing atmospheric pressure.

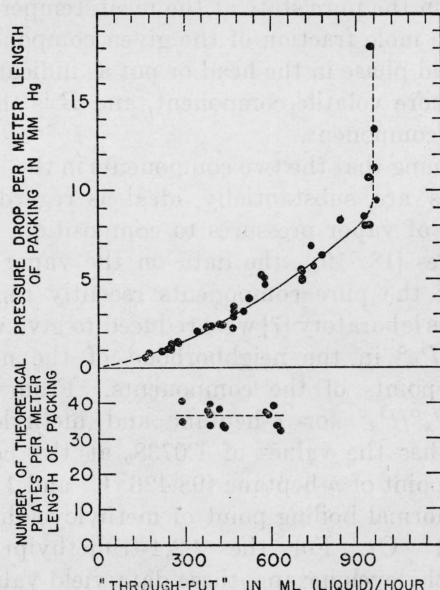


FIGURE 15.—Results of performance tests on rectifying section of 15-mm diameter packed with stainless-steel helices.

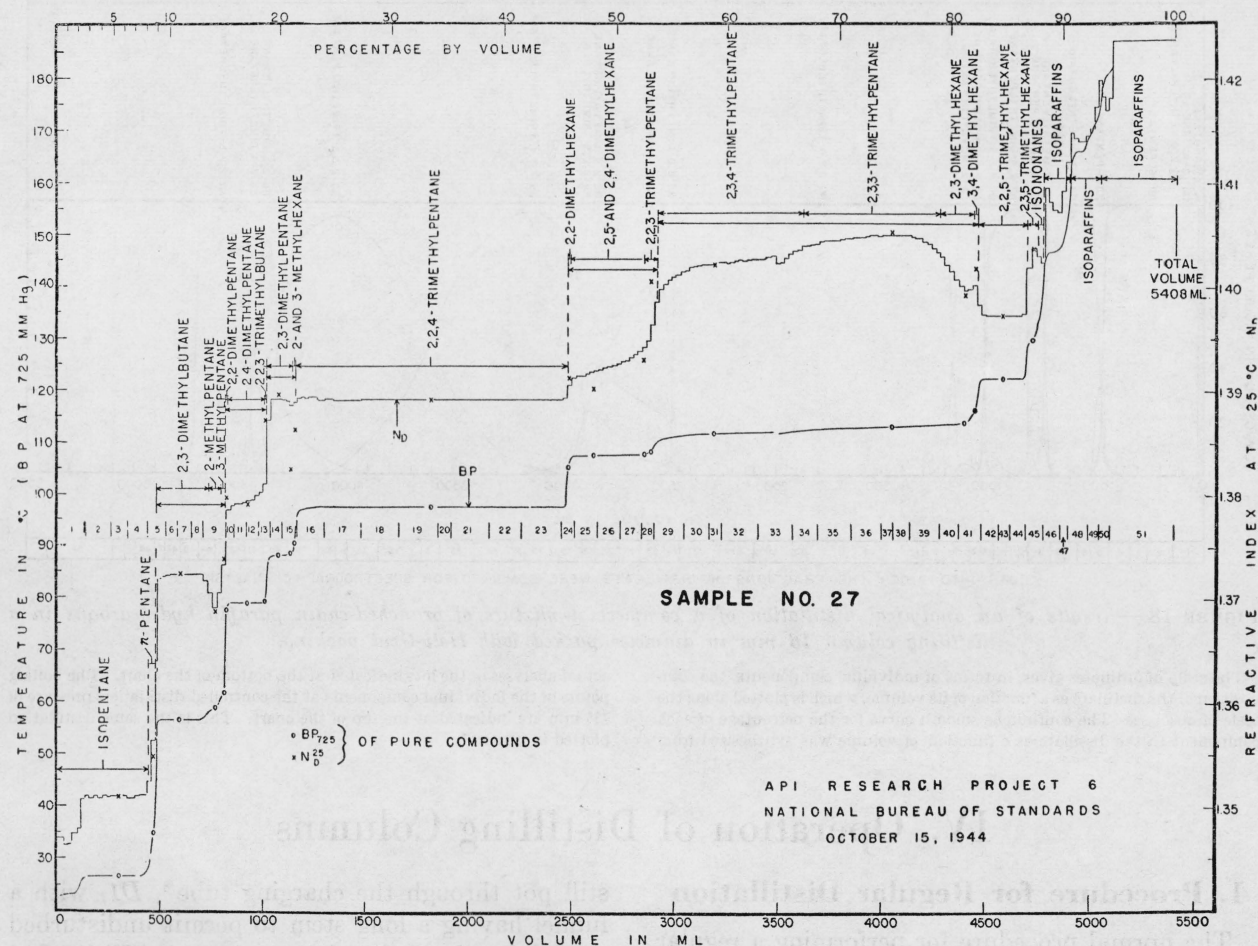
The upper scale of ordinates gives the pressure drop, in mm Hg, per meter length of packing; the lower scale of ordinates gives the number of equivalent theoretical plates per meter length of packing; and the scale of abscissas gives the "through-put" in milliliters (liquid) per hour. The rectifying section of the distilling column in which these tests were made was 15 mm in inside diameter and 2.71 m in length, and was packed with stainless-steel helices, $\frac{3}{32}$ inch in diameter, No. 30 AWG wire [5]. The test mixture was methylcyclohexane plus 2,2,4-trimethylpentane. The measurements of pressure drop were performed at a controlled pressure of 770 mm at the head of the column. The mean value of the number of equivalent theoretical plates is 36.4, with an average deviation of ± 2.1 . Determination of the number of equivalent theoretical plates was made at the prevailing atmospheric pressure.

FIGURE 16.—Results of performance tests on rectifying section of 25-mm diameter packed with stainless-steel helices.

The upper scale of ordinates gives the pressure drop, in mm Hg, per meter length of packing; the lower scale of ordinates gives the number of equivalent theoretical plates per meter; and the scale of abscissas gives the "through-put" in milliliters (liquid) per hour. The rectifying sections of the five different distilling columns in which these tests were made were as follows: Column *E*, points marked X; column *F*, points marked ■; and column *G*, points marked □, inside diameter of 25 mm and length of 2.75 m; column *M*, points marked ●; and column *N*, points marked △, inside diameter of 25 mm and length of 2.73 m. The test mixtures were methylcyclohexane plus 2,2,4-trimethylpentane for columns *E*, *F*, *M*, and *N*, and methylcyclohexane plus *n*-heptane for column *G*. For pressure drop, curves I, II, and III give results for controlled pressures of 770, 217, and 57 mm Hg, respectively, at the head of the column. The mean value of the number of equivalent theoretical plates is 33.2, with an average deviation of ± 1.6 . Determination of the number of equivalent theoretical plates was made at the prevailing atmospheric pressure.

FIGURE 17. Results of an analytical distillation of a commercial mixture of branched-chain paraffin hydrocarbons in a distilling column of 16-mm diameter, packed with Heli-Grid packing.

One scale of ordinates gives, as indicated, the temperature of the liquid-vapor equilibrium at the head of the column under a controlled pressure of



725 mm Hg. The other scale of ordinates gives the refractive index, N_D , at 25° C, of the fractions (18 ml) of distillate collected. The scale of abscissas gives the volume of the distillate in milliliters. The data were analyzed [15] to give the components indicated in the upper part of the chart. This distillation was performed in column 4, which has a rectifying section 16 mm in diameter with 3.66 m of Heli-Grid packing [3], under the following conditions,

with preflooding of the column at the start of the distillation: Time allowed for attainment of equilibrium at start, 24 hours; rate of removal of distillate, 4.5 ml/hour; pressure drop, 18.6 mm Hg; calculated reflux ratio 150/1; controlled pressure, 725 mm Hg; total elapsed time, 1,087 hours. The numbers in the lower part of the chart refer to lots in which the fractions of distillate were blended for spectrographic analysis. (See text and fig. 17.)

sure drop of 10 mm Hg and a calculated throughput of 340 ml an hour. This gives 51 equivalent theoretical plates, and a pressure drop of 5.5 mm Hg, per meter length of packing at this throughput. Although the values of the number of equivalent theoretical plates per meter length of this packing is appreciably less than that reported by Podbielniak [3], it is still very favorably large. Another advantageous characteristic of the Heli-Grid packing is its low hold-up per equivalent theoretical plate.

In figure 17 are plotted the results of an analytical distillation of a commercial petroleum product consisting essentially of a mixture of branched-chain paraffin hydrocarbons C_5 to C_9 . Complete

details of this test are given in the legend of figure 17.

The fractions of distillate from the above-mentioned distillation were subsequently blended into larger lots, as indicated by the horizontal row of numbers through the lower middle of figure 17. These lots of material were analyzed for the actual amounts of the individual components by means of infrared spectrographic analysis in the Research Laboratory of the Socony-Vacuum Oil Co., Paulsboro, N. J. Figure 18 is a plot of the results giving the composition of the distillate in terms of individual components as interpreted from the infrared spectrographic analyses. Details are given in the legend of figure 18.

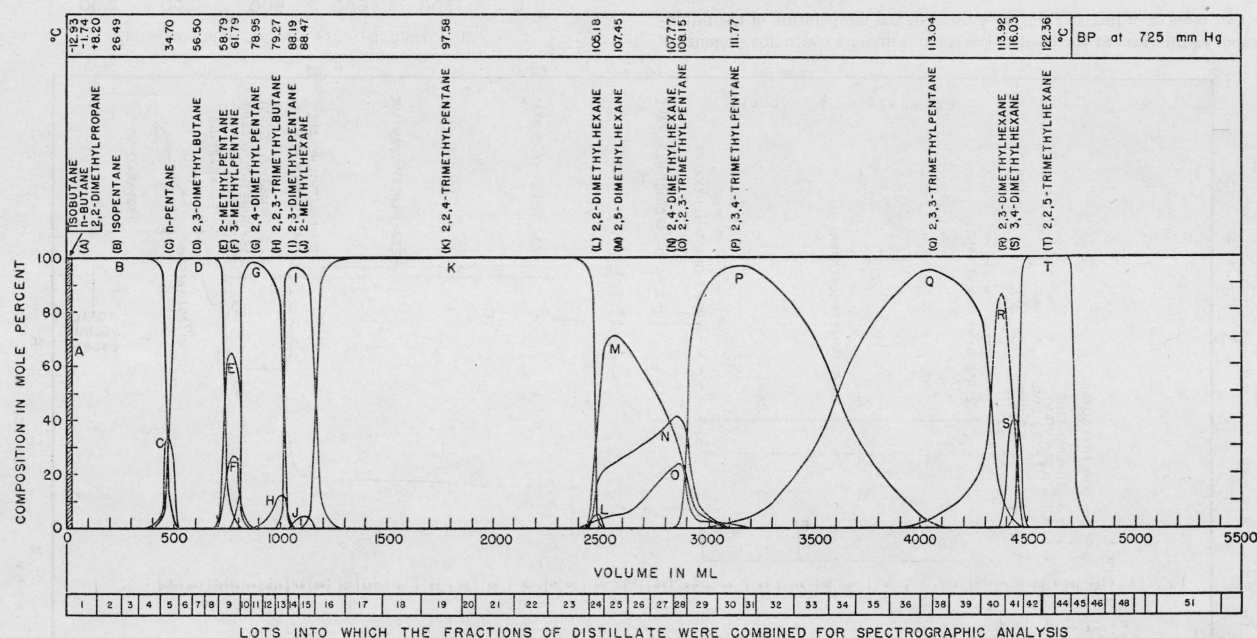


FIGURE 18.—Results of an analytical distillation of a commercial mixture of branched-chain paraffin hydrocarbons in a distilling column 18 mm in diameter packed with Heli-Grid packing.

The scale of ordinates gives, in terms of individual components, the composition of the distillate as a function of its volume, which is plotted along the scale of abscissas. The continuous smooth curve for the percentage of each component in the distillate as a function of volume was synthesized from

actual analyses of the lots indicated at the bottom of the chart. The boiling points of the individual components at the controlled distillation pressure of 725 mm are indicated at the top of the chart. This is the same distillation plotted in figure 17.

IV. Operation of Distilling Columns

1. Procedure for Regular Distillation

The normal procedure for performing a regular distillation at one of the controlled pressures is as follows:

The material to be charged is appropriately cooled, if volatile, and then introduced into the

still pot through the charging tube⁸, *D1*, with a funnel having a long stem to permit undisturbed exit of the air displaced from the pot. The reflux regulator, *A1*, at the head of the column is closed;

⁸ The letters and numbers following in the text in this section refer to figure 1, unless otherwise stated.

the rates of flow of water through the condenser, *A4*, at the head and those at the receiving assembly, *E7* and *E8*, are adjusted; and the valve to the proper controlled pressure is opened.

The electric current is switched on to the pot heaters and, if necessary (see below), to the jacket of the column. For material boiling below about 50° C at the given pressure, no heating is applied to the jacket. For material boiling between 50° and about 150° C at the given pressure, the electric power is applied simultaneously to pot and jacket heaters. For material normally boiling above about 150° C, electric power is applied to the jacket heaters about 1 hour in advance of the pot heaters. This procedure reduces the difference in temperature between the inside and outside of the rectifying section at the time boiling starts and throws less strain on the expansion elements in the vacuum-jacketed rectifying section. The variable transformers controlling the power to each section of the jacket are initially set to produce a maximum temperature about 10° C below the initial boiling point of the material.

Following the usual practice with packings of the kind used in these columns, the rectifying section is flooded at the start [3, 11] by adding sufficient extra heat to the pot to force liquid into the head of the column. As soon as flooding occurs, the electric power to the pot is reduced and compressed air, *D18*, is introduced into the pot assembly to accelerate cooling.

When the pressure drop through the column decreases to a value below the normal operating pressure drop (previously selected on the basis of the desired through-put), the electric power to the pot heaters is adjusted to normal, and the electric relay control system is connected. This relay controls the upper or intermittent one of the two pot heaters. The lower pot heater is on continuously, but is set at a power input that is not quite enough to maintain the required through-put. The upper pot heater, controlled by the relay circuit, *E4*, figure 9, through the mercury manometer, *E15*, supplies power intermittently to maintain the pressure drop through the column at the constant preselected value. As the temperature of the material being distilled increases, additional power is required to be added to the lower pot heater which is on continuously.

The temperature of the metal tube, *B5*, in the jacket assembly is manually controlled by means of variable transformers, *A2*, *B2*, and

C2 in figure 9, so that the temperatures at the bottom, top, and middle thermometer wells, *B7*, are maintained as follows: The bottom, *G3* in figure 9, at the same temperature as the material in the pot (preferably the temperature of the liquid returning to the pot) *G4*, fig. 9; the top, *G1*, in figure 9, at the same temperature as the liquid-vapor equilibrium in the head, *F1* in figure 9; and the middle, *G2* in figure 9, at the mean of the top and bottom temperatures. As the metal tube is separated from the material inside the rectifying section by an air gap, *C* in figure 7, and a silvered, evacuated, jacket, *B* in figure 7, its temperature need be controlled only within 1 or 2 degrees of the desired value.

After the through-put, as measured by the pressure drop, reaches its normal operating value, the column is operated at total reflux for a period of from 24 to 36 hours to permit attainment of equilibrium in the rectifying section.

Following the period of establishment of equilibrium, an initial setting of the metal regulator, *A1*, and glass valve, *A5*, at the reflux regulator is made on the basis of the time of fall of 1 drop at the drop counter, *A10*. (For this purpose, 1 drop of hydrocarbon material of the gasoline range is assumed to be equal to 0.04 ml). Adjustment of this rate to the prescribed value is subsequently made on the basis of the actual hourly increment of volume of liquid in the receiver, *E14*.

At the prescribed intervals of time, the product in the receiver is removed as a "fraction." In this operation, the receiver is isolated from the column by closing the stopcocks *E10* and *E11*, and then opened to the atmosphere by opening stopcock *E12*. The material is carefully withdrawn from the bottom of the receiver through stopcock *E16*, with appropriate drainage from the tip of the receiver into the receiving bottle. After the material has been carefully capped, the stopcocks *E16* and *E12* are closed, and stopcocks *E10* and *E11* are opened to the column, slowly in order to permit the air in the receiver to be reduced to the operating pressure without disturbing the operation of the column.⁹

Up to the time that the still reaches its normal operating through-put after flooding, the operations have been conducted by the supervisor or assistant supervisor of the distillation laboratory.

⁹ For very low pressures, a separate evacuating system may be used to bring the receiver to the operating pressure before it is reopened to the column.

From this point on, the operation of the distilling column is turned over to the distillation operator, who may have as many as 15 of the distilling columns to care for. The laboratory has one distillation operator on duty each shift of 8 hours, with the distilling columns being operated 24 hours a day, 7 days a week.

The assignment sheets for each new distillation prescribe the pressure at which the distillation is to be performed, the normal operating pressure drop, the rate of collection of product, the size of the "fractions" to be collected, and the time interval between collection of fractions.

The distillation operator checks each of the distilling columns once every hour, making the following observations and entering them on printed record sheets:

(a) The resistance of the platinum thermometer giving the temperature of the liquid-vapor equilibrium in the head is measured. This resistance is recorded accurately to the nearest 0.001 ohm (equivalent to 0.01 degree centigrade).

(b) The foregoing resistance is converted roughly to degrees centigrade from a table giving average values of resistance with respect to temperature for the 15 platinum thermometers in the system. This conversion¹⁰ is made roughly, for purposes of operation, with a precision of 0.1 degree centigrade and an accuracy of about one-half degree.

(c) The volume of the liquid in the receiver is recorded, to 0.1 ml or 0.01 ml, depending upon the size of the receiver.

(d) The hourly increment of volume in the receiver, obtained by subtraction of the preceding volume in the receiver, is recorded, for the purpose of checking adherence to the prescribed rate of collection of product.

(e) The pressure drop through the column, as measured on the oil manometer, *E13*, is recorded to 0.1 cm.

(f) The emf of the three thermoelements giving the temperatures of the top, middle, and bottom of the metal tube in the jacket assembly, and of the one thermoelement giving the temperature of the pot, are measured.

(g) These emf are converted to temperature in degrees centigrade, recording to the nearest 1.0 degree.

¹⁰ After the distillation is completed, the record of the temperature of the liquid-vapor equilibrium is given to the appropriate research investigator, who makes the conversion of the temperature of the liquid-vapor equilibrium accurately to 0.01 degree from the individual table for the given platinum thermometer used.

(h) Appropriate adjustments to the settings of the variable transformers controlling the power to the lower pot heater and to the three sections of the jacket are made.

(i) The scale readings (voltage) on the five variable transformers controlling the two pot heaters and the three jacket heaters are recorded.

As the end of the distillation approaches, an accurate comparison is made of the volume of material collected and the volume charged, to permit a reliable estimate of the day on which the distilling column will be shut down. Normally, the distillation is halted when the rapid fall of the pressure drop from its normal operating value indicates depletion of the liquid in the pot. At this point, the valve to the controlled pressure system is closed, all electric power is cut off, and the pot and jacket are allowed to cool to room temperature. The cooling of the pot is accelerated by a flow of air into the pot assembly, *D18*. After the pot has cooled, the residue is withdrawn from the pot through the withdrawal tube (see *D*, fig. 3) inserted down through the charging tube, *D1*, in close proximity to the recess in the bottom of the pot. (See *G*, fig. 3.)

After the residue has been removed, acetone is charged to the pot and distilled at total reflux to clean out the column. After the acetone is removed, air is drawn through the pot and rectifying section to "dry out" the column. Before the next distillation the stopcocks on the receiving assembly are cleaned and relubricated, normally with tetraethylene glycol citrate [16].

2. Procedure for Azeotropic Distillation

The procedure followed in the operation of the distilling columns for azeotropic distillation is the same as for the regular distillation described in the preceding section except that, normally, an excess of the added azeotrope-forming substance is added to the hydrocarbon charge in the pot and the distillation is carried through to the point where no hydrocarbon remains in the columns, as evidenced by the rise of the temperature of the liquid-vapor equilibrium in the head to that corresponding to the pure azeotrope-forming substance. The operator is normally instructed to halt the distillation when there have been collected two fractions with boiling points equal to that of the azeotrope-forming substance at the given pressure.

V. Conclusion

As of December 31, 1945, the 15 distilling columns assembled in the distillation room described in section II-3 and figures 12 and 13 of this report had the characteristics shown in table 1. It is planned to make improvements in the apparatus

and equipment as new information from this and other laboratories becomes available. The earlier distilling apparatus in this laboratory is described in reference [17].

TABLE 1.—Characteristics of the 15 distilling columns installed as of December 31, 1945

Number of distilling column ^a	Rectifying section			Pot		Minimum operating residue (approximate)	Operating pressure drop	Operating throughput	Rate of collection of product	Operating reflux ratio (approximate)	Estimated number of theoretical plates (at total reflux)
	Diameter	Length	Packing ^b	Actual volume	Maximum charging capacity						
	mm	m		Liters	Liters	ml	mm Hg	ml/hour	ml/hour		
1.....	11	2.74	HG	3.2	2.7	40	12.1	300	2.0	150/1	150
2.....	13	1.83	HG	7.2	6.0	50	8.5	300	2.2	135/1	100
3 ^c	13	1.83	HG	7.2	6.0	50	8.5	300	2.2	135/1	100
4.....	16	3.66	HG	7.2	6.0	100	19.2	720	4.0	180/1	200
5.....	25	3.66	SSH	18.0	15.0	300	21.3	1,560	12.5	125/1	125
6.....	25	3.66	SSH	18.0	15.0	300	21.3	1,560	12.5	125/1	125
7.....	20	3.66	SSH	7.2	6.0	135	21.3	1,240	8.5	145/1	130
8.....	20	3.66	SSH	7.2	6.0	135	21.3	1,240	8.5	145/1	130
9.....	15	3.66	SSH	7.2	6.0	100	21.3	740	4.5	165/1	135
10.....	15	3.66	SSH	7.2	6.0	100	21.3	740	4.5	165/1	135
11A.....	16	3.66	HG	7.2	6.0	100	19.2	720	4.0	180/1	200
12.....	15	3.66	SSH	3.2	2.7	80	21.3	740	4.5	165/1	135
13.....	20	3.66	SSH	7.2	6.0	135	21.3	1,240	8.5	145/1	130
14.....	25	3.66	SSH	7.2	6.0	175	21.3	1,560	12.5	125/1	125
15 ^c	25	3.66	SSH	7.2	6.0	175	21.3	1,560	12.5	125/1	125

^a "A" attached to the number of the distilling column indicates that the original rectifying section was changed. The rectifying section in the original column 11 was one of the same length 10 mm in diameter packed with the stainless steel helices described in footnote "b".

^b SSH represents stainless-steel helices, $\frac{3}{16}$ inch in diameter, made of No. 30 AWG wire [5]; HG represents Heli-Grid packing [3].

^c Columns 3 and 15 are planned to be changed so that their rectifying sections will be similar to that of column 4.

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results of their infrared spectrographic analysis of the fractions of the distillate shown in figures 17 and 18.

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